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Oxidative Dehydrogenation of Ethane over MoVTeNbO Catalyst Prepared by a Slurry Method

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The oxidative dehydrogenation (ODH) of ethane to ethene has attracted much attention in recent years. López Nieto *et al*[1] reported that MoVTeNbO catalysts prepared by hydrothermal synthesis show high activity and selectivity for ODH of ethane, and an ethene yield of 75 % was obtained at 400 ℃ on the best catalysts. In ethane oxidation, the catalytic behavior of MoVTeNbO catalysts can be mainly related to the presence of the multifunctional $Te_2M_{20}O_{57}$ orthorhombic phase in cooperation with the (V, Nb)-containing Mo_5O_{14}-type phase[2,3].

In this paper, we report the preparation of the MoVTeNbO catalyst by a slurry method, its characterization and the influence of the calcination atmosphere on the catalyst performance for the ODH of ethane.

The MoVTeNbO catalyst was prepared by a slurry method. Ammonium heptamolybdate, ammonium metavanadate and telluric acid were dissolved upon heating to 80 ℃ in a flask, and niobium oxalate was dissolved in another flask. The atomic ratio of Mo∶V∶Te∶Nb was 1∶0.3∶0.23∶0.1. The aqueous solution of niobium oxalate was added to the first flask to result in a slurry. The water in this slurry was removed by a rotary evaporator to obtain the precursor solid. After it was dried at 80 ℃ for 10 h, the precursor solid was calcined at 600 ℃ for 2 h in a N_2 stream (the sample is denoted as SL-N). For comparison, the same precursor solid was calcined at 600 ℃ for 2 h in air (denoted as SL-A).

The catalytic performance of the MoVTeNbO catalyst for the ODH of ethane was tested in a fixed-bed quartz tubular reactor at atmospheric pressure. The result is shown in Table 1. SL-N showed good catalytic performance for the ODH of ethane to ethene at reaction temperatures above 400 ℃, and ethene was formed as the main product. The ethane conversion increased and the selectivity for ethene decreased with increasing temperature. A maximum ethene yield of 80.9 % was achieved at 440 ℃ on SL-N. However, on SL-A almost no activity for the ODH of ethane was detected.

Table 1 ODH of ethane on MoVTeNbO catalyst samples

Sample	t/ ℃	X/ %	S/ %			Y/ %
			C_2H_4	CO	CO_2	
Blank	440	—	—	—	—	—
SL-N	400	59.0	95.4	0.8	3.8	56.3
	420	75.5	93.6	1.4	5.0	70.7
	440	89.6	90.3	1.5	8.2	80.9
	460	95.8	83.4	3.9	12.8	79.9
SL-A	440	—	—	—	—	—

Reaction conditions: 500 mg catalyst, total flow rate 10 ml/ min, feed composition 30 %C_2H_6-30 %O_2-40 %N_2.

XRD patterns of the MoVTeNbO catalyst are shown in Fig 1. SL-A was primarily composed of the MoO_3 phase but no MoO_3 was observed in the pattern of SL-N. SL-N gave peaks at 2θ = 7.7°, 9.0°, 22.1°, 26.2°, 26.8°, 27.3°, 29.2° and 35.4°, which were mainly related to an orthorhombic $Te_2M_{20}O_{57}$ (M = Mo, V and Nb) phase, while peaks

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at 7.7°, 8.7°, 14.0°, 22.1°, 23.3°, 24.9°, 29.7°, 31.5°, 32.4° and 33.5° were attributed to $(Mo_{0.93}V_{0.07})_5O_{14}$ [JCPDS, 31-1437] and/or $Nb_{0.09}Mo_{0.91}O_{2.80}$ [JCPDS, 27-1310] or $Mo_{5-x}(V/Nb)_xO_{14}$-like phases. The peaks at 22.1°, 28.2°, 36.2°, 45.2° and 50.0° were assigned to the $Te_{0.33}MO_3$ (M = Mo, V, and Nb) phase[2~4].

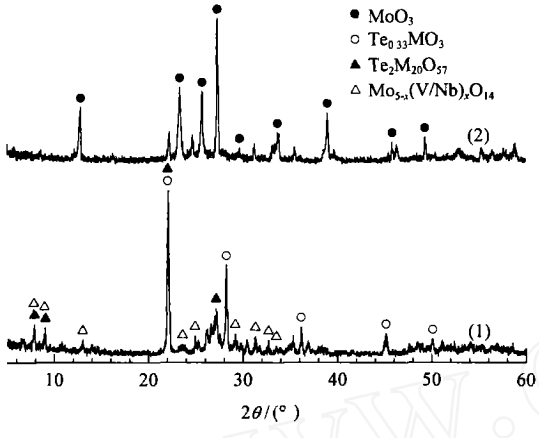

Fig 1 XRD patterns of solid MoVTeNbO catalyst samples
(1) SL-N, (2) SL-A

The difference in the surface morphology of the two samples was revealed by SEM, as shown in Fig 2. SL-A has plate-like structure with fairly smooth surfaces, while SL-N has a porous surface morphology with some fine structure, which was in good agreement with the surface area measurements. The BET specific surface area of SL-N was 6.92 m^2/g, while that of SL-A was only 0.31 m^2/g. This result also agreed with the finding by Watanabe *et al*[5] that a higher surface area of the catalyst correlated well with a higher catalytic activity.

In conclusion, the MoVTeNbO catalyst prepared by the slurry method and calcined at 600 ℃ in a N_2 stream exhibits an ethane conversion of 90 % and an ethene selectivity of 90 % at 440 ℃. A highly crystalline MoVTeNbO catalyst may be one of the most effective catalysts for ethene production using low cost ethane.

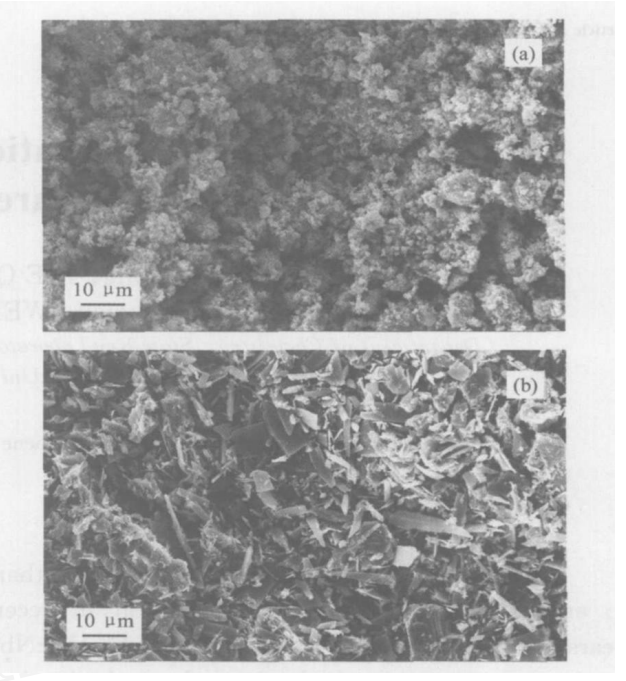

Fig 2 SEM images of MoVTeNbO catalyst samples
(a) SL-N, (b) SL-A

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浆态法制备的 MoVTeNbO 催化剂上的乙烷氧化脱氢

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摘要: 采用浆态法在 N_2 气氛下焙烧制得了 $MoV_{0.3}Te_{0.23}Nb_{0.1}O_x$ 催化剂. 在以该催化剂催化的乙烷氧化脱氢制乙烯的反应中, 440 ℃下乙烷的转化率和乙烯的选择性均在 90 %左右, 乙烯产率达 80.9 %. 但在空气气氛下焙烧得到的催化剂几乎没有催化活性. 用 XRD 和 SEM 等方法考察了催化剂的结构.

关键词: 乙烷, 氧化脱氢, 乙烯, 氧化钼, 氧化钒, 氧化碲, 氧化铌, 混合金属氧化物催化剂

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